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<p>(54) Title: CATALYSTS FOR THE SELECTIVE OXIDATION OF CARBON MONOXIDE IN HYDROGEN-CONTAINING GASES</p> <p>(57) Abstract</p> <p>The invention relates to a method for the selective catalytic oxidation of carbonmonoxide (CO) in H₂-rich, CO₂- and H₂-containing gases in the presence of a noble metal catalyst on an alumina carrier with the addition of air as oxidising agent. According to the invention, with this method α-Al₂O₃ is used as carrier material. The specific surface area of the α-Al₂O₃ carrier can be less than 25 m²/gram. The noble metal can be ruthenium or platinum and preferably a combination of ruthenium (Ru) and platinum (Pt), the sum of the quantities of Ru and Pt being less than or equal to 1.0 % (m/m).</p>		

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Catalysts for the selective oxidation of carbon monoxide in hydrogen-containing gases

Introduction/background information

The invention relates to a method for the selective catalytic oxidation of carbon
5 monoxide (CO) in the presence of a noble metal catalyst on an alumina carrier.

Fuel cells are being investigated in many places as a possible energy source for driving
vehicles and for stationary generation of electricity. The use of fuel cells is still highly
dependent on the availability of the fuel: hydrogen (H₂). It is not to be expected that an
infrastructure for hydrogen will be set up within the foreseeable future. Especially for mobile
10 applications, it is therefore necessary to transport an available fuel, or a fuel that becomes
available, and to convert this to hydrogen as the feed for the fuel cell.

A gas mixture that consists mainly of hydrogen and carbon dioxide (CO₂) is then
produced - for example via steam reforming and/or partial oxidation - from fuels such as
methane, LPG, methanol, petrol, diesel and other hydrocarbons. Said gas mixture, which is
15 rich in hydrogen, is then fed to the fuel cell which generates electricity by an electrochemical
reaction of hydrogen with oxygen.

However, a certain amount of carbon monoxide (CO) is also always liberated during
the conversion of said fuels into hydrogen. For instance, a gas mixture of, for example,
75 % (V/V) H₂, 24 % (V/V) CO₂ and 1 % (V/V) CO is produced on steam reforming of
20 methanol. A solid polymer fuel cell, the major candidate for transport applications, is
extremely sensitive to CO, which even in low concentrations (0.01 % (V/V)) has an adverse
effect on the performance of the fuel cell. For a usable system it is therefore necessary to
remove CO down to the said level and preferably down to a lower level (< 0.005 % (V/V),
50 ppm). A technically attractive option for removing CO from H₂-containing gas streams is
25 by means of selective oxidation of CO to CO₂ at low temperature (100 °C - 200 °C). In this
context it is important that the consumption of hydrogen by non-selective oxidation to water
is minimised.

The power of ruthenium (Ru) to catalyse the oxidation of CO is, for example, known
from the ammonia synthesis process. Thus, it is known from US Patent 3 216 782 (9
30 November 1965) that 0.5 % (m/m) Ru on alumina (Al₂O₃) is capable of oxidising
0.055 - 0.6 % (V/V) CO in the presence of H₂ at between 120 °C and 160 °C to a level of less
than 15 ppm. In this case it is necessary that the quantity of oxygen (O₂) added is such that
the molar O₂/CO ratio is between 1 and 2. The excess oxygen which is not needed for the

oxidation of CO reacts with hydrogen to give water. It has not been investigated whether this Ru catalyst is also capable of oxidising CO from a typical reformat gas to a CO level of 15 ppm under the same conditions (temperature, O₂/CO ratio).

In the Journal of Catalysis 142 (1993), Academic Press Inc., pages 257-259, S.H. Oh and R.M. Sinkevitch describe 0.5 % (m/m) Ru/ γ -Al₂O₃ as highly effective in the complete oxidation, at low temperature (100 °C), of 900 ppm CO with 800 ppm oxygen (O₂) in a gas mixture which also contains 0.85 % (V/V) H₂, with the remainder being N₂. Data on the stability of the Ru catalyst are not given in the article and in addition the behaviour of the catalyst in a realistic reformat gas containing H₂, CO₂, H₂O and CO in much higher concentrations was not investigated.

Current state of the art

European Patent EP 0 743 694 A1 (20 November 1996) refers to an oxidation unit for the selective oxidation of CO in H₂-rich gas at a reaction temperature of between 80 °C and 100 °C. A molar ratio of O₂/CO of 3 is used. The final CO content is a few ppm. The excess oxygen reacts with hydrogen to give water. The catalyst consists of a 0.2 % (m/m) - 0.5 % (m/m) Pt-Ru alloy on Al₂O₃. No examples which would show the stability of the catalyst are given.

US Patent 5 674 460 (7 October 1997) describes a structured reactor for the catalytic removal of CO from H₂-rich gas at between 90 °C and 230 °C. Depending on the temperature, the catalyst in this case consists of Pt on γ -Al₂O₃, Pt on zeolite-Y or Ru on γ -Al₂O₃. The invention is explained solely on the basis of 5 % (m/m) Pt on γ -Al₂O₃, by means of which the CO content can be reduced to about 40 ppm at a reaction temperature of between 80 °C and 130 °C. No stability data are given in this patent either.

In the Journal of Catalysis 168 (1997), Academic Press, pages 125-127, R.M. Torres Sanchez et al. describe gold on manganese oxide as an alternative catalyst for the oxidation of CO in H₂ at low temperatures (approximately 50 °C). In particular the price, due to the high gold loading (approximately 4 - 10 % (m/m)), makes the use of this type of catalyst less interesting. Moreover, this type of catalyst is able to withstand carbon dioxide to only a limited extent.

It is not clear from the above whether the catalysts of the prior art are suitable for the selective oxidation of CO in H₂-rich reformat gas mixtures where there is high activity in conjunction with good stability in the temperature range 100 °C - 200 °C and where a low

oxygen excess can be used to minimise the hydrogen consumption.

Discovery of new catalyst

One aim of the present invention is to provide a method for the selective catalytic
5 oxidation of CO from H₂-rich, CO₂- and H₂O-containing (reformate) gas mixtures, making
use of as small as possible an amount of oxygen and at relatively low temperature. A further
aim of the present invention is to provide a catalyst which has high chemical and thermal
stability and can be produced in a cost-effective manner by means of a simple method of
preparation from commercially available starting materials and a low noble metal loading.

10 The use of commercially available α -Al₂O₃ as carrier material in the preparation of
0.5 % (m/m) Ru on Al₂O₃ led, surprisingly, to a catalyst which in the temperature range
120 °C - 160 °C combines high activity (> 99% conversion of CO) with high stability (a CO
conversion of at least 97 % for a period of at least 50 hours) in the oxidation of CO with a
relatively small excess of oxygen in dilute reformate gas. These results were found to be
15 appreciably better than the results which were obtained with a commercially available
0.5 % (m/m) ruthenium catalyst with γ -Al₂O₃ as the carrier (specific surface area > 100 m²/g),
which is representative of the catalysts used in the abovementioned studies and reflects the
prior art.

It has also been found that the addition of Pt and the lowering of the total noble metal
20 loading resulted in a catalyst which showed even better stability for the selective oxidation of
CO in both dilute and undiluted reformate gas (a CO conversion of at least 99 % for a period
of at least 50 hours).

It has furthermore been found that in particular the nature and the specific surface area
of the Al₂O₃ carrier used are the factors determining the exceptional performance of the Ru
25 and Ru-Pt catalysts according to the present invention. Preferably, alumina is used in the form
of α -Al₂O₃. A highly active and stable catalyst is formed when the specific surface area of the
 α -Al₂O₃ is in the range from 3 m²/g to 25 m²/g.

The catalysts in the present invention can be prepared in a simple manner via a standard
impregnation method from commercially available starting materials. Compared with the
30 current state of the art, the method according to the present invention has the following
advantages:

- complete oxidation of CO to CO₂ in the temperature range 120 °C to 160 °C with only a
small excess of oxygen (O₂/CO = 1) compared with the stoichiometrically required quantity

of oxygen ($O_2/CO = 0.5$),

- minimal hydrogen consumption as a result of low oxygen excess ($O_2/CO = 1$),
- stable action at 130 °C in simulated reformat gas (0.5 % (V/V) CO, 0.5 % (V/V) O_2 , 74 % (V/V) H_2 , 19 % (V/V) CO_2 and 6 % (V/V) H_2O) for a period of at least 50 hours
- 5 (residual quantity of CO < 50 ppm),
- low noble metal loading of less than 0.5 % (m/m).

$\alpha-Al_2O_3$ is a commercial product that is used, inter alia, in the electronics industry in the production of thick and thin substrate layers by tape casting. Another application is the production of industrial ceramics.

- 10 The use of this $\alpha-Al_2O_3$ as carrier for a selective oxidation catalyst for CO in H_2 -rich gas mixtures has not been described before.

The invention will be explained in more detail on the basis of the following examples together with the appended figures.

- 15 In the figures:

Figure 1 shows the activity of a 0.5 % (m/m) Ru-on- $\alpha-Al_2O_3$ catalyst (code A1Ru-5) compared with the activity of a commercial Ru catalyst with 0.5 % (m/m) Ru on $\gamma-Al_2O_3$ (code G1RuC-5) in the oxidation of CO in dilute reformat gas,

- 20 Figure 2 shows the stability of A1Ru-5 in the CO oxidation at 130 °C compared with the stability of G1RuC-5 in dilute reformat gas,

Figure 3 shows the activity of a 0.25 % (m/m) Ru, 0.125 % (m/m) Pt-on- $\alpha-Al_2O_3$ catalyst (code A1RuPt-48) compared with the activity of A1Ru-5 in the oxidation of CO in dilute reformat gas,

- 25 Figure 4 shows the stability of A1RuPt-48 in the CO oxidation at 130 °C compared with the stability of A1Ru-5 in dilute reformat gas,

Figure 5 shows the activity of A1RuPt-48 in the oxidation of CO as a function of the reformat gas composition,

Figure 6 shows the stability of A1RuPt-48 in the CO oxidation at 130 °C as a function of the reformat gas composition and

- 30 Figure 7 shows the activity of A2RuPt-48 compared with the activity of A1Ru-5 and G3Ru-5 in the oxidation of CO in undiluted reformat gas.

In the following tests the Ru-on- $\alpha-Al_2O_3$ and the Ru-Pt-on- $\alpha-Al_2O_3$ catalysts were prepared by impregnation of a commercial $\alpha-Al_2O_3$ carrier with solutions of the salts

5 ruthenium nitrosyl nitrate and hexachloroplatinic acid. The effect of the α -Al₂O₃ carrier on the CO oxidation activity and stability of the catalyst is determined under III below. The effect of the addition of Pt and the lowering of the total noble metal loading on the catalyst activity and stability is given under IV. Finally, the activity and the stability of the catalyst as a function of the composition of the reformat gas are determined under V.

I. Preparation of Ru-on- α -Al₂O₃ and Ru-Pt-on- α -Al₂O₃ catalysts

The catalysts according to the present invention were prepared by dry impregnation of α -Al₂O₃ powder with solutions of ruthenium nitrosyl nitrate ((Ru(NO)(NO₃)_x(OH)_y (x+y=3),
10 Ru content of the solution 1.5 % (m/m)) and hexachloroplatinic acid (H₂PtCl₆.xH₂O), Pt content 0.5 % (m/m)).

The 0.5 % (m/m) Ru-on- α -Al₂O₃ catalyst (code A1Ru-5) was prepared by adding 5 gram of the Ru solution to 15 gram of the α -Al₂O₃ powder in a glass beaker and then stirring well until a pasty substance was formed. This paste was then dried in air in an oven for 16
15 hours at 80 °C. During drying the setting paste was stirred several times. After drying, the solid material was finely ground to a homogeneous powder with the aid of a mortar. The powder thus produced was then pressed to give a pill. After crushing the pill in a mortar a 0.25 mm to 0.5 mm sieve fraction was prepared for the catalytic measurements. The catalyst prepared was stored in a polyethylene sample bottle at room temperature.

20 In the case of the 0.25 % (m/m) Ru and 0.125 % (m/m) Pt-on- α -Al₂O₃ catalysts (codes A1RuPt-48 and A2RuPt-48), first 1.68 gram of the Ru solution and then 2.51 gram of the Pt solution were added to 10 gram of the α -Al₂O₃ powder. The subsequent preparation steps were identical to those described above for A1Ru-5.

25 II. Test apparatus and test procedure

The conversion of CO was studied in an automated micro-flow set-up operating under atmospheric pressure. The following gases were available to the set-up: N₂, O₂, H₂, CO₂, CO and H₂O. It was possible to measure the gases H₂, CO₂ and CO with the aid of a Perkin-Elmer model 8500 gas chromatograph equipped with a methanizer, connected in series, a
30 TCD and an FID. A pneumatically controlled 6-way tap was used for sampling the product gas. CO was also measured occasionally with an Elsag Bailey Hartmann & Braun model URAS 10E ND-IR analyser.

The precursor was contained in a Pyrex glass reactor having an internal diameter of

10 mm. The catalyst bed was covered with glass wool and a layer of glass beads. The height of the catalyst bed was approximately 5 mm, whilst the gas flow was approximately 75 ml/min. The space velocity (SV) was approximately $11,000 \text{ h}^{-1}$ in this case. The amount of precursor required (0.25 mm - 0.5 mm fraction) was 200 or 400 mg. The temperature was
5 measured immediately below the catalyst bed using a CrAl thermocouple.

During the measurements the catalyst sample was exposed to a pre-mixed gas containing 0.5 % (V/V) CO, 0.5 % (V/V) O₂, 5 or 19 % (V/V) CO₂, 15, 51 or 74 % (V/V) H₂, 6 or 7 % (V/V) H₂O, with the remainder being N₂. Prior to the CO oxidation measurement the catalyst sample was pre-treated with, successively, air at 400 °C and 25 % (V/V) H₂ in N₂
10 at 550 °C for activation. The activated catalyst was then cooled under H₂/N₂ to the starting temperature for the test. The reactor was flushed with N₂ for approximately 10 minutes each time the gas composition was changed. For activity measurements the starting temperature was always 80 °C, after which the reactor temperature was raised in 10 °C steps to a final temperature of 250 °C. The CO conversion was determined at each temperature. For stability
15 measurements the catalyst bed was first brought to the measurement temperature under H₂/N₂ after the pretreatment, after which the CO conversion was determined once an hour for a period of 50 hours. The general test conditions for the CO oxidation measurements are given in Table 1.

The CO conversion was calculated on the basis of the amount of CO in the product gas
20 (CO_{out}) using the GC and the amount of CO in the feed gas (CO_{in} = 0.5 % (V/V)) determined using the GC in accordance with: $\text{CO conversion (in \%)} = 100 + (\text{CO}_{\text{in}} - \text{CO}_{\text{out}})/\text{CO}_{\text{in}}$. Using the NDIR it was separately determined that the detection limit of the GC for CO was approximately 25-30 ppm.

Table 1 General test conditions

Weight of catalyst sample	200-400 mg
Volume of catalyst bed	approx. 0.4 - 0.6 ml
Particle size	0.25-0.50 mm
Gas flow rate	75 ml/min
Spatial velocity of the gas per hour (GHSV)	10,000 - 15,000 h ⁻¹
Feed gases	
Reformate gas 1	0.5% CO, 0.5% O ₂ , 15% H ₂ , 5% CO ₂ , 7% H ₂ O, remainder N ₂
Reformate gas 2	0.5% CO, 0.5% O ₂ , 51% H ₂ , 5% CO ₂ , 7% H ₂ O, remainder N ₂
Reformate gas 3	0.5% CO, 0.5% O ₂ , 74% H ₂ , 19% CO ₂ , 6% H ₂ O
Total pressure	atmospheric
Temperature of catalyst bed	80 °C - 250 °C (10 °C steps in the activity measurements) 130 °C (stability measurements)

III. Effect of α -Al₂O₃ carrier on CO oxidation in dilute reformate gas

The test results for the oxidation of CO with O₂ in dilute reformate gas (gas 1) over the Ru-on-alumina catalyst (code A1Ru-5) show that the use of α -Al₂O₃ as the carrier for Ru results in both a better activity and a better stability in the oxidation of CO compared with a commercial Ru-on- γ -Al₂O₃ catalyst (code G1RuC-5).

Figure 1 shows the activity of A1Ru-5 compared with the activity of G1RuC-5 in the oxidation of CO in dilute reformate gas 1. Catalyst A1Ru-5 achieves a more complete CO conversion over a wider temperature range than does G1RuC-5.

Figure 2 shows the stability in the CO oxidation in dilute reformate gas 1 with A1Ru-5 compared with the stability of G1RuC-5. A1Ru-5 is found to be both more active and more stable in the CO oxidation than G1RuC-5 over a measurement period of 50 hours.

IV. CO oxidation in dilute reformate gas with Ru-Pt on α -Al₂O₃

Test results for the oxidation of CO with O₂ in dilute reformate gas 1 over a Ru-Pt-on- α -Al₂O₃ catalyst (code A1RuPt-48) demonstrate that the addition of Pt and lowering the total noble metal loading results in a catalyst which is more stable than the A1Ru-5 described above. The addition of platinum and lowering the total noble metal loading was not found to have a significant effect on the activity of the catalyst.

Figure 3 shows the activity of A1RuPt-48, which has a low loading, compared with the activity of A1Ru-5 in the oxidation of CO in dilute reformat gas 1. It can clearly be seen that from 120 °C A1RuPt-48 shows virtually the same CO conversion as a function of the temperature as A1Ru-5. This is despite the lower noble metal loading of A1RuPt-48 compared with A1Ru-5.

Figure 4 shows the stability of A1RuPt-48 in the CO oxidation at 130 °C compared with the stability of A1Ru-5 in dilute reformat gas 1. A1RuPt-48 displays a higher conversion of CO than A1Ru-5 over the entire measurement period.

10 V. Effect of reformat gas composition on CO oxidation with Ru-Pt on α -Al₂O₃

Test results for the oxidation of CO with O₂ in various reformat gases 1, 2 and 3 over the Ru-Pt-on- α -Al₂O₃ catalyst described above show that activity and stability are virtually independent of the composition of the reformat gas.

Figure 5 shows the activity of A1RuPt-48 in the oxidation of CO measured in various reformat gas compositions. Only at the highest temperatures is the conversion of CO in the less dilute reformat gases 2 and 3 somewhat lower than the conversion in the most dilute reformat gas 1.

Figure 6 shows the stability of A1RuPt-48 in the CO oxidation in the three different reformat gases 1, 2 and 3. The very high CO conversion with this catalyst is dependent to only a very slight extent on the composition of the reformat gas; even with simulated undiluted reformat gas 3 there is more than 99% CO conversion over the entire measurement period (residual quantity of CO < 50 ppm).

Figure 7 shows the activity of three catalysts in the oxidation of CO in undiluted reformat gas 3. The various curves in Figure 7 for 0.5 % (m/m) Ru on γ -Al₂O₃ (code G3Ru-5), 0.5 % (m/m) Ru on α -Al₂O₃ (code A1Ru-5) and 0.25 % (m/m) Ru and 0.125 % (m/m) Pt on α -Al₂O₃ (code A2RuPt-48) show the substantial effect of the type of carrier material (γ compared with α) and the metal composition (Ru compared with Ru/Pt).

Claims

1. Method for the selective catalytic oxidation of carbon monoxide (CO) in H₂-rich, CO₂- and H₂O-containing gases in the presence of a noble metal catalyst on an alumina carrier with the addition of air as oxidising agent, characterised in that α -Al₂O₃ is used as carrier material.
5
2. Method according to Claim 1, characterised in that the specific surface area of the α -Al₂O₃ carrier is less than 25 m²/gram.
- 10 3. Method according to Claim 1, characterised in that the noble metal is ruthenium or platinum and preferably a combination of ruthenium (Ru) and platinum (Pt).
4. Method according to Claims 1 and 3, characterised in that the sum of the quantities of Ru and Pt is less than or equal to 1.0 % (m/m).
15
5. Method according to Claim 1, characterised in that the quantity of air added to the gas stream to be treated corresponds to a quantity of oxygen which in molar terms is at most five times as great as the quantity of CO to be removed and preferably is equal to the quantity of CO to be removed and is at least equal to half the quantity of CO to be removed.
20
6. Method according to Claim 1, characterised in that the oxidation takes place at a temperature of between 100 °C and 200 °C, preferably of between 120 °C and 180 °C.
- 25 7. Method according to Claims 1 and 6, characterised in that the temperature at which the oxidation takes place is maintained by using the catalyst in or on a reactor which has the features of a heat exchanger.

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fig-1

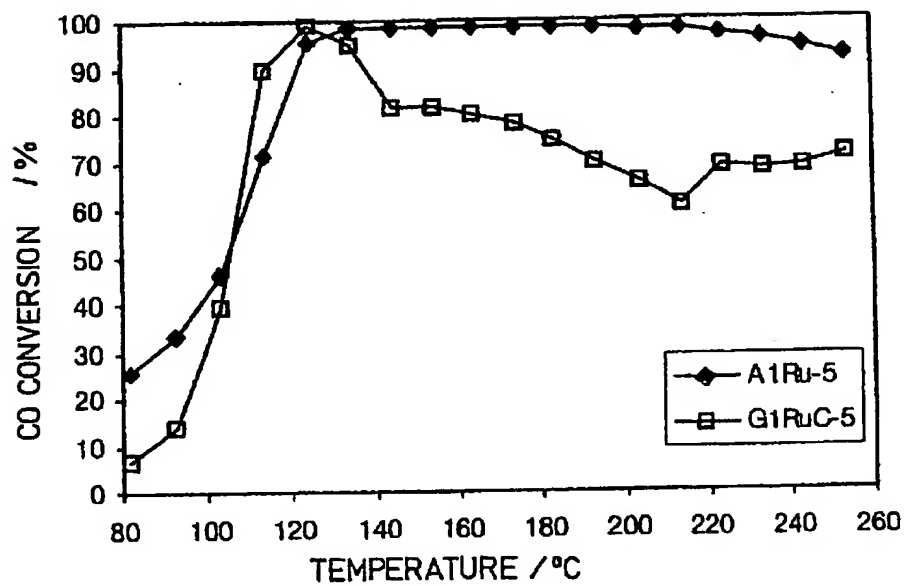
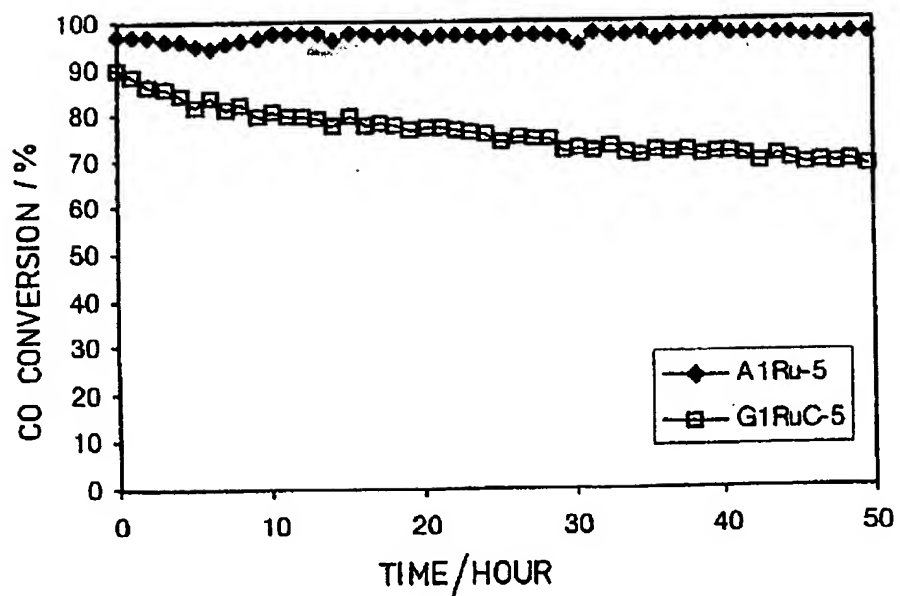


fig-2



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fig-3

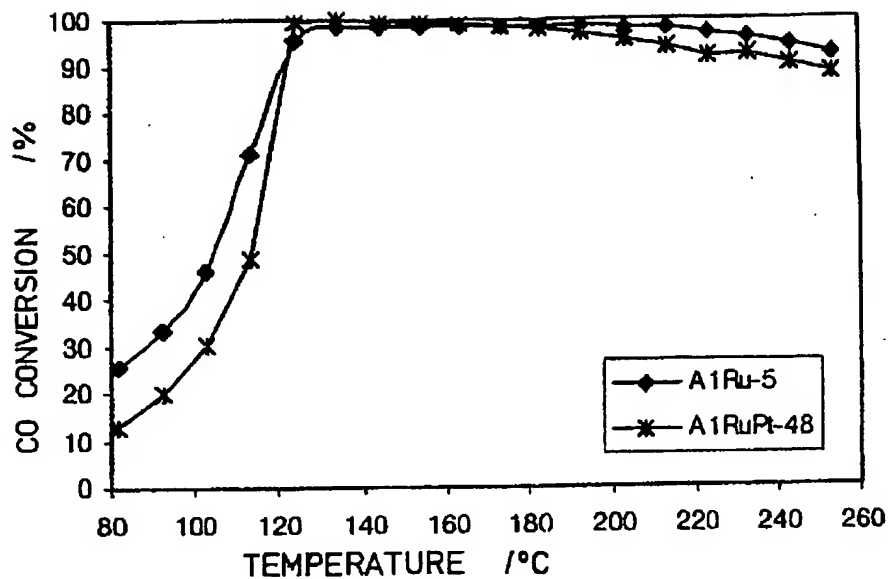
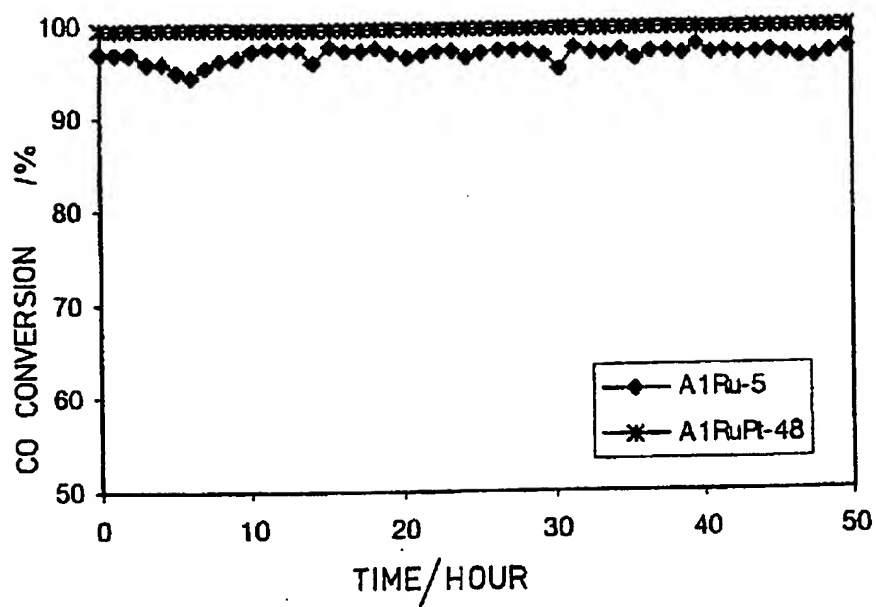


fig-4



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fig- 5

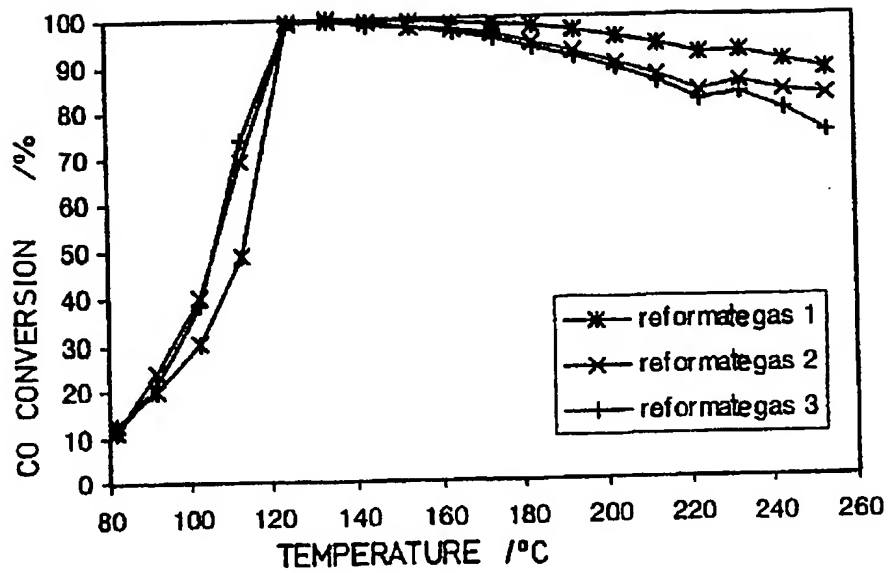
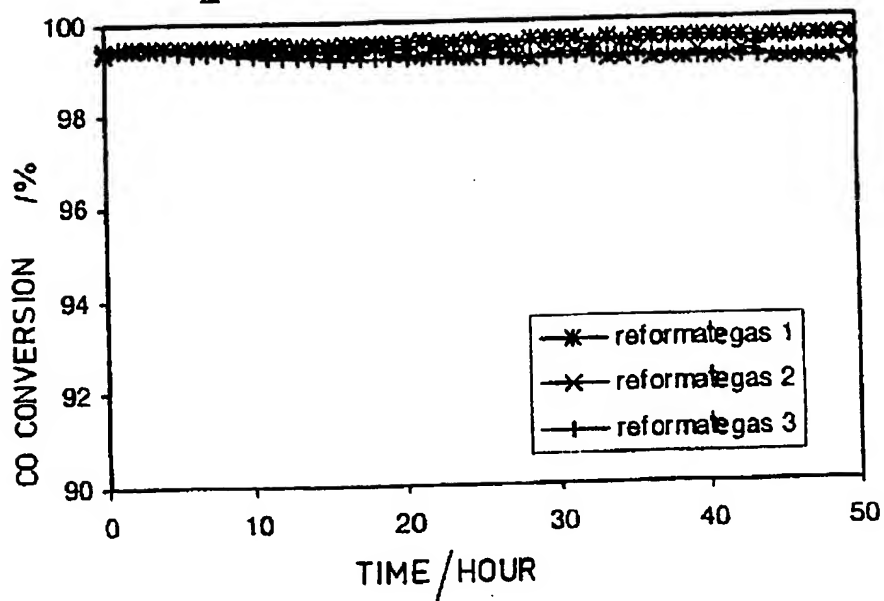
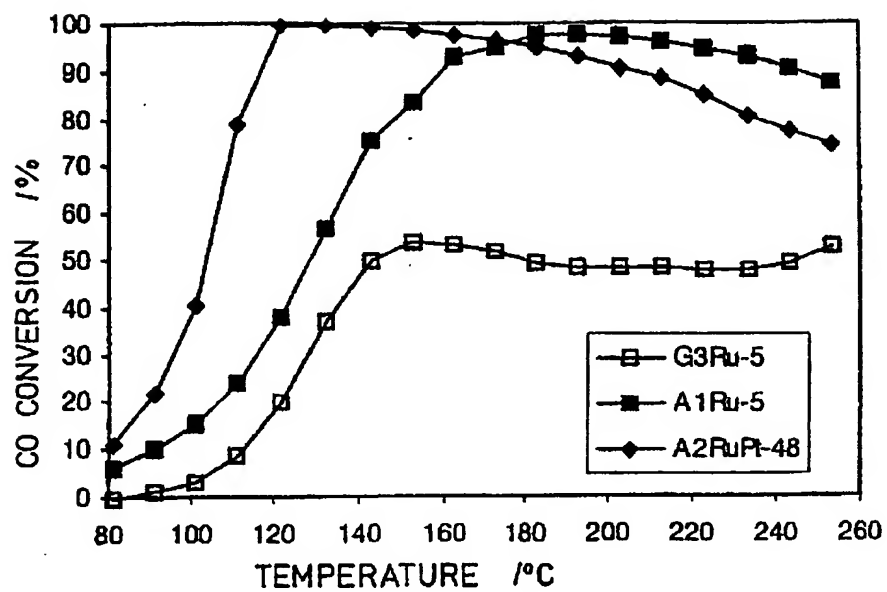


fig- 6



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fig- 7



INTERNATIONAL SEARCH REPORT

Inter: 1st Application No
PCT/NL 99/00584

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C01B3/58		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C01B 801D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 43 34 983 A (DAIMLER-BENZ) 20 April 1995 (1995-04-20) claims	1-7
A	US 5 491 120 A (KENNETH E. VOS ET AL.) 13 February 1996 (1996-02-13) column 2, line 16 -column 3, line 42; claims	1-7
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INTERNATIONAL SEARCH REPORT

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